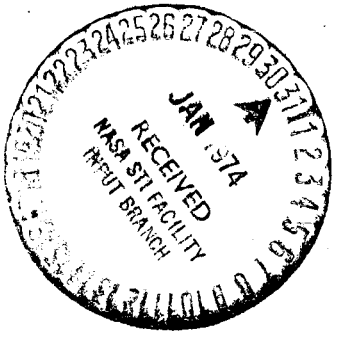
TWENTY-THIRD SEMI-ANNUAL PROGRESS REPORT TO NATIONAL AERONAUTICS AND SPACE ADMINISTRATION (THEORETICAL CHEMISTRY INSTITUTE PORTION)

1 July 1973 - 31 December 1973



MISC. 102

31 December 1973

NASA RESEARCH GRANT NGL 50-002-001

SEMI-ANNUAL REPORT FOR PERIOD

1 July 1973 - 31 December 1973

Submitted by:

Joseph O. Hirschfelder, Theoretical Chemistry Institute

UNIVERSITY OF WISCONSIN

MADISON

NASA SEMI-ANNUAL PROGRESS REPORT

The University of Wisconsin Theoretical Chemistry Institute is an integral part of the Department of Chemistry and has excellent working arrangements with the Physics, Mathematics, Computer Sciences and various Engineering Departments. Most of the permanent staff members hold joint appointments with these departments. In addition to their research, these staff members carry normal teaching loads and take their teaching responsibilities very seriously. In addition to graduate courses, they also teach undergraduate courses in elementary physical chemistry (laboratory as well as lecture), thermodynamics and reaction kinetics. We believe that our teaching program in theoretical chemistry is one of the best.

As a result of the NASA grant, the University of Wisconsin has been able to expand its theoretical chemistry faculty. We have noticed that the sharp improvement in the caliber of new graduate students and the quality of applicants of postdoctoral appointments at the Theoretical Chemistry Institute is continuing. In addition, a number of eminent professors are choosing to come to Wisconsin both for summer leaves and for sabbatical years in order to take advantage of the opportunities available at the Theoretical Chemistry Institute.

At the present time, we have 2 professors of chemistry, 1 professor of physics, 1 associate professor of physics, 1 associate professor of chemistry, 1 assistant professor of chemistry, and 1 visiting associate professor of chemistry (June 1, 1973 - September 30, 1973). We have 1 postdoctoral associate, and 13 graduate students, including 6 research assistants (supported by NASA funds), 6 research assistants (supported by NSF funds), and 1 teaching assistant (U.W.-supported). These do not

include the experimental students and postdoctoral associates working under Professor Harriman.

At this time before reviewing the progress of the latest semi-annual period, we want to express our appreciation to the National Aeronautics and Space Administration (NASA) for providing the Theoretical Chemistry Institute with the opportunity for developing an excellent teaching and research program. Although NASA has not contributed any "new" money to the support of the Theoretical Chemistry Institute since 1970, we have made use of the "shingling" funds in our grant to continue with our NASA-supported research. The University of Wisconsin has also liberally contributed to the program of the members, awarding teaching assistantships and graduate fellowships to many of our graduate students and providing very excellent computing facilities.

We are indeed fortunate that the National Science Foundation has been helping to finance our research since fiscal 1970 when NASA stopped giving us additional financial support. The "shingling" funds which NASA had already appropriated to our grant are helping a great deal to make this transition possible.

RESEARCH INTERESTS OF THE THEORETICAL CHEMISTRY INSTITUTE STAFF

There is a wide range of research at the Theoretical Chemistry Institute. Saul T. Epstein, Phillip R. Certain and Joseph O. Hirschfelder are currently working on molecular and intermolecular quantum mechanics problems. C. F. Curtiss is concerned with the theory of statistical mechanics, transport properties, and molecular collisions. John E. Harriman is working on electron spin resonance and quantum mechanical density matrices. The following is a summary of the detailed interests of each of the staff members.

SIE-SIE- 84) REV. 6-64

NOT FOR PUBLICATION OR PUBLICATION REFERENCE

NOTICE OF RESEARCH PROJECT
SCIENCE INFORMATION EXCHANGE
SMITHSONIAN INSTITUTION

SIE NO.

AGENCY NO.

SUPPORTING AGENCY: NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
Office of University Affairs
Sustaining University Program

TITLE OF PROJECT:
THE SPONTANEOUS IONIZATION OF A HYDROGEN ATOM IN AN ELECTRIC FIELD

Give names, departments, and official titles of PRINCIPAL INVESTIGATORS and ALL OTHER PROFESSIONAL PERSONNEL engaged on the project.

Joseph O. Hirschfelder, Director Theoretical Chemistry Institute and Professor of Chemistry

Arturo Hardisson, Visiting Associate Professor, Theoretical Chemistry Institute

Albert Christoph, Research Assistant, Theoretical Chemistry Institute

NAME AND ADDRESS OF INSTITUTION:
Theoretical Chemistry Institute, University of Wisconsin, 1101 University Avenue, Madison, Wisconsin 53706

SUMMARY OF PROPOSED WORK – (200 words or less.) – In the Science Information Exchange summaries of work in progress are exchanged with government and private agencies supporting research, and are forwarded to investigators who request such information. Your summary is to be used for these purposes. (Please indicate the number of students supported by this project.)

This research has been going on for a long time. Currently we are considering the effects of relativistic interactions which arise in the Dirac Hamiltonian together with possible radiative processes. The relativistic corrections may have a profound change on the lifetime of some of the quantum states since these corrections destroy the separability of the system in parabolic coordinates. At the present time we can calculate the energies and lifetimes corresponding to the electrostatic Hamiltonian. We have completed the formal aspects of the relativistic corrections and will soon start the actual computing machine calculations.

The first phase of this work was published by Joseph O. Hirschfelder and Larry Curtiss in the Journal of Chemical Physics 55, 1395 (1971). In June 1971, George Hart prepared a preliminary report (WIS-TCI-445G) entitled "Square Well Model Calculations of Rate Ionization of Metastable Atomic States", which provides a simple idealization of the hydrogen atom spontaneous ionization and shows in a simple way exactly how the Wigner-Weisskopf model works and what are its limitations. This research should be of considerable interest with respect to the spectroscopy of Stellar atmospheres.

SIGNATURE OF PRINCIPAL INVESTIGATOR: Joseph O. Hirschfelder

PROFESSIONAL SCHOOL (medical, graduate, etc.): Theoretical Chemistry Institute
University of Wisconsin-Madison

ANNUAL FUNDING *	NUMBER OF	PERIOD OF AUTHORIZATION
Faculty	Faculty	Date Initiated:
Students		
Other	Students	Completion Date:
Total	Publications	

*include overhead

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NOTICE OF RESEARCH PROJECT
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AGENCY NO.

5

SUPPORTING AGENCY:
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
Office of University Affairs
Sustaining University Program

TITLE OF PROJECT:
TWO-DIMENSIONAL REFLECTION AND TUNNELING OF QUANTUM MECHANICAL WAVES

Give names, departments, and official titles of PRINCIPAL INVESTIGATORS and ALL OTHER PROFESSIONAL PERSONNEL engaged on the project.
Joseph O. Hirschfelder, Director Theoretical Chemistry Institute and Professor of Chemistry

Albert Christoph, Research Assistant, Theoretical Chemistry Institute

NAME AND ADDRESS OF INSTITUTION:
Theoretical Chemistry Institute, University of Wisconsin, 1101 University Avenue, Madison, Wisconsin 53706

SUMMARY OF PROPOSED WORK – (200 words or less.) – In the Science Information Exchange summaries of work in progress are exchanged with government and private agencies supporting research, and are forwarded to investigators who request such information. Your summary is to be used for these purposes. (Please indicate the number of students supported by this project.)

There is considerable interest at the present time in the use of semi-classical quantum mechanical or generalized WKB methods for treating both reactive and non-reactive molecular collisions. One of the principle approximations involved is the use of the stationary phase approximation (or method of steepest descent). This approximation has the effect of approximating "wave" optics by "ray" optics. In optics and in microwaves, it is recognized that the stationary phase assumption is valid when the wave length is small compared to the dimensions of the optical system. The question is how valid is its use in molecular collisions where the wave packets are quite diffuse and the deBroglie wave length is rapidly varying.

We have made exact calculations of Debye-Picht wave packets hitting a simple, two-dimensional, plane barrier and found that the stationary phase approximation accurately gives the displacement of the reflected and the transmitted waves. The displacement of the reflected wave corresponds to the Goos-Hänchen effect in optics, and the transmitted wave corresponds to the "frustrated total reflection" effect in optics.

In the course of this work we have discovered a family of quantized vortices which will require further investigation.

SIGNATURE OF PRINCIPAL INVESTIGATOR: Joseph O. Hirschfelder

PROFESSIONAL SCHOOL (medical, graduate, etc.): Theoretical Chemistry Institute
University of Wisconsin-Madison

ANNUAL FUNDING *	NUMBER OF	PERIOD OF AUTHORIZATION
Faculty	Faculty	Date Initiated:
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Other	Students	Completion Date:
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SIE NO.

AGENCY NO.

SUPPORTING AGENCY:
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
Office of University Affairs
Sustaining University Program

TITLE OF PROJECT:
ROTATIONAL EXCITATION IN COLLISIONS OF DIATOMIC MOLECULES

Give names, departments, and official titles of PRINCIPAL INVESTIGATORS and ALL OTHER PROFESSIONAL PERSONNEL engaged on the project.

C.F. Curtiss, Associate Director Theoretical Chemistry Institute and Professor of Chemistry

NAME AND ADDRESS OF INSTITUTION:
Theoretical Chemistry Institute, University of Wisconsin, 1101 University Avenue
Madison, Wisconsin 53706

SUMMARY OF PROPOSED WORK – (200 words or less.) – In the Science Information Exchange summaries of work in progress are exchanged with government and private agencies supporting research, and are forwarded to investigators who request such information. Your summary is to be used for these purposes. (Please indicate the number of students supported by this project.)

For some time we have considered the theory of rotational excitation in collisions of diatomic molecules. These results have now been generalized to the scattering of polyatomic molecules, and we have considered in particular the special case of symmetric top molecules in which the moment of inertia about the symmetry axis is small. The scattering of such molecules was considered by a perturbation method based on the scattering of diatomic molecules. The formal perturbation development is discussed in a paper which recently appeared in the Journal of Chemical Physics. In this paper a distorted wave approximation for the T-matrix for atom-symmetric top scattering is developed which is correct to first order in the part of the interaction potential which leads to transitions in the component of the rotational atom momentum along with symmetry axis. In a more recent report, WIS-TCI-499, which has been accepted for publication in the Journal of Chemical Physics, a semi-classical approximation to this T-matrix is derived.

SIGNATURE OF PRINCIPAL INVESTIGATOR C.F. Curtiss

PROFESSIONAL SCHOOL (medical, graduate, etc.) University of Wisconsin Theoretical Chemistry Institute

ANNUAL FUNDING *	NUMBER OF	PERIOD OF AUTHORIZATION
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Total		

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AGENCY NO.

7

SUPPORTING AGENCY:
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
Office of University Affairs
Sustaining University Program

TITLE OF PROJECT:

1/Z EXPANSION FOR ATOMS.

Give names, departments, and official titles of PRINCIPAL INVESTIGATORS and ALL OTHER PROFESSIONAL PERSONNEL engaged on the project.

P. R. Certain, Assistant Professor, Theoretical Chemistry Institute
R. Ray, Research Assistant, Theoretical Chemistry Institute

NAME AND ADDRESS OF INSTITUTION:

University of Wisconsin, Theoretical Chemistry Institute
1101 University Avenue, Madison, Wisconsin 53706

SUMMARY OF PROPOSED WORK – (200 words or less.) – In the Science Information Exchange summaries of work in progress are exchanged with government and private agencies supporting research, and are forwarded to investigators who request such information. Your summary is to be used for these purposes. (Please indicate the number of students supported by this project.)

The 1/Z expansion for atomic binding energies is of the form

$$E = Z^2(E_0 + E_1/Z + E_2/Z^2 + \dots)$$

We are considering the three-electron isoelectronic series and will compute the coefficients E_2, E_3, E_4, E_5 for the ground and low-lying excited states. We will also consider the radius of convergence of the series, and the Z^{-1} expansion of atomic properties other than the energy.

SIGNATURE OF PRINCIPAL INVESTIGATOR P.R. Certain

University of Wisconsin

PROFESSIONAL SCHOOL (medical, graduate, etc.) Theoretical Chemistry Institute

ANNUAL FUNDING *	NUMBER OF	PERIOD OF AUTHORIZATION
Faculty	Faculty	Date Initiated:
Students		
Other	Students	Completion Date:
Total	Publications	

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AGENCY NO.

7a

SUPPORTING AGENCY:
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
Office of University Affairs
Sustaining University Program

TITLE OF PROJECT:
DIPOLE MOMENTS OF EXCITED STATE MOLECULES

Give names, departments, and official titles of PRINCIPAL INVESTIGATORS and ALL OTHER PROFESSIONAL PERSONNEL engaged on the project.

P. R. Certain, Assistant Professor, Theoretical Chemistry Institute
Jeanne Fromm, Research Assistant, Theoretical Chemistry Institute
William Halchin, Research Assistant, Theoretical Chemistry Institute

NAME AND ADDRESS OF INSTITUTION:
University of Wisconsin, 1101 University Avenue
Theoretical Chemistry Institute, Madison, Wisconsin 53706

SUMMARY OF PROPOSED WORK – (200 words or less.) – In the Science Information Exchange summaries of work in progress are exchanged with government and private agencies supporting research, and are forwarded to investigators who request such information. Your summary is to be used for these purposes. (Please indicate the number of students supported by this project.)

We are calculating self-consistent-field dipole moments of molecules in singlet and triplet excited states with the aim of developing rules of thumb which allow predictions of the results on the basis of the ground state properties of the molecule.

SIGNATURE OF PRINCIPAL INVESTIGATOR R. R. Certain
University of Wisconsin

PROFESSIONAL SCHOOL (medical, graduate, etc.) Theoretical Chemistry Institute

ANNUAL FUNDING *	NUMBER OF	PERIOD OF AUTHORIZATION
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Other	Students	Completion Date:
Total		
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SIE NO.

AGENCY NO.

SUPPORTING AGENCY: NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
Office of University Affairs
Sustaining University Program

TITLE OF PROJECT:

Give names, departments, and official titles of PRINCIPAL INVESTIGATORS and ALL OTHER PROFESSIONAL PERSONNEL engaged on the project.

Saul T. Epstein, Professor, Theoretical Chemistry Institute

John O. Eaves, Research Assistant, Theoretical Chemistry Institute

NAME AND ADDRESS OF INSTITUTION:
Theoretical Chemistry Institute, University of Wisconsin-Madison, 1101 University Avenue, Madison, Wisconsin 53706

SUMMARY OF PROPOSED WORK – (200 words or less.) – In the Science Information Exchange summaries of work in progress are exchanged with government and private agencies supporting research, and are forwarded to investigators who request such information. Your summary is to be used for these purposes. (Please indicate the number of students supported by this project.)

During this period I have continued to be concerned with my book (The Variation Method in Quantum Chemistry) which is now in the proof reading stage.

Also John Eaves, a pre-doctoral student, has started to work with me on a mathematical problem which arises in many SCF approximations.

SIGNATURE OF PRINCIPAL INVESTIGATOR Saul T Epst

PROFESSIONAL SCHOOL (medical, graduate, etc.) University of Wisconsin ~~Theoretical Chemistry Institute~~

ANNUAL FUNDING *	NUMBER OF	PERIOD OF AUTHORIZATION
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Other	Students	Completion Date:
Total	Publications	

*include overhead

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SMITHSONIAN INSTITUTION

SIE NO.

AGENCY NO.

9

SUPPORTING AGENCY:
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
Office of University Affairs
Sustaining University Program

TITLE OF PROJECT:
DENSITY MATRICES AND SPIN PROPERTIES

Give names, departments, and official titles of PRINCIPAL INVESTIGATORS and ALL OTHER PROFESSIONAL PERSONNEL engaged on the project.

John E. Harriman, Associate Professor, Theoretical Chemistry Institute

NAME AND ADDRESS OF INSTITUTION:
University of Wisconsin, Theoretical Chemistry Institute, 1101 University Avenue, Madison, Wisconsin 53706

SUMMARY OF PROPOSED WORK – (200 words or less.) – In the Science Information Exchange summaries of work in progress are exchanged with government and private agencies supporting research, and are forwarded to investigators who request such information. Your summary is to be used for these purposes. (Please indicate the number of students supported by this project.)

Work is not currently being supported by NASA. Several projects represent a continuation of work which has previously received some NASA support.

1. Theory and properties of reduced density matrices. Particular attention is now being given to symmetry properties, and to the geometric characterization of the subspace of density matrices within the space of Hermitian, trace 1 matrices.

2. Calculations are being done on the three-electron system and LiH^+ with particular attention to the way in which spin density distributions change with changing internuclear distance. (Tortorelli)

SIGNATURE OF PRINCIPAL INVESTIGATOR: John E. Harriman

PROFESSIONAL SCHOOL (medical, graduate, etc.): University of Wisconsin / Theoretical Chemistry Institute

ANNUAL FUNDING *	NUMBER OF	PERIOD OF AUTHORIZATION
Faculty	Faculty	Date Initiated:
Students		
Other	Students	Completion Date:
Total		
	Publications	

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SIE NO.

AGENCY NO.

10

SUPPORTING AGENCY:

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
Office of University Affairs
Sustaining University Program

TITLE OF PROJECT:

RELATIVISTIC EFFECTS IN MANY-ELECTRON SYSTEMS

Give names, departments, and official titles of PRINCIPAL INVESTIGATORS and ALL OTHER PROFESSIONAL PERSONNEL engaged on the project.

John Detrich, Project Associate, Theoretical Chemistry Institute

NAME AND ADDRESS OF INSTITUTION:

Theoretical Chemistry Institute, University of Wisconsin-Madison, 1101 University Avenue, Madison, Wisconsin 53706

SUMMARY OF PROPOSED WORK – (200 words or less.) – In the Science Information Exchange summaries of work in progress are exchanged with government and private agencies supporting research, and are forwarded to investigators who request such information. Your summary is to be used for these purposes. (Please indicate the number of students supported by this project.)

I am working on a problem which I started in collaboration with Professor C. C. J. Roothaan at the University of Chicago; I developed a formalism suitable for the treatment of relativistic effects in complex atoms and molecules. This formalism can be used to treat many of the higher-order relativistic effects which are not included in the Breit-Pauli approximation. However, some higher-order effects were omitted by avoiding second quantization of the electron field. I am currently extending the formalism to include such effects. This work should be of great interest to the understanding of hyper-fine structure in molecules and to second-order effects in NMR and ESR.

SIGNATURE OF PRINCIPAL INVESTIGATOR _____

PROFESSIONAL SCHOOL (medical, graduate, etc.) University of Wisconsin Theoretical Chemistry Institute

ANNUAL FUNDING *	NUMBER OF	PERIOD OF AUTHORIZATION
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Students	Students	Completion Date:
Other	Publications	
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SUMMARY OF RESEARCH AT THE THEORETICAL CHEMISTRY INSTITUTE

DURING THE PERIOD 1 JULY 1973 THROUGH 31 DECEMBER 1973

THERMODYNAMIC FUNCTIONS OF MOLECULAR HYDROGEN FROM AB INITIO ENERGY LEVELS by R. Kosloff, R. D. Levine, and R. B. Bernstein
WIS-TCI-493 (supported by NASA) 9 July 1973
This manuscript has been accepted for publication in Molecular Physics.

ABSTRACT

A tabulation is presented of the thermodynamic properties of molecular hydrogen (H_2, D_2 and HD), calculated using energy levels which had been obtained via a solution of the Schrödinger equation. The present results should be more accurate than prior computations based on spectroscopic extrapolation formulas. They provide the first example of an accurate determination of a bulk, macroscopic property directly from first principles (input: masses and Coulomb's law).

The results are tabulated for ortho, para, the equilibrium and the frozen (or "normal") mixture (3:1 for H_2, 1:2 for D_2) over the temperature range 5-300°K and for the frozen mixture up to 6000°K.

The importance of anharmonicity and of quasibound levels at high temperatures is discussed.

ANALYSIS OF ENERGY DISPOSAL: THERMODYNAMIC ASPECTS OF THE ENTROPY DEFICIENCY OF A PRODUCT STATE DISTRIBUTION by R. D. Levine and R. B. Bernstein
WIS-TCI-494 (supported by NASA) 13 July 1973
Chem. Phys. Lett. 22, 217-221 (1973).

ABSTRACT

A thermodynamic-like approach to the characterization of product state distributions is outlined. A moment analysis of the surprisal and the entropy deficiency is presented from a statistical mechanical viewpoint. The role of reactant state selection is discussed using the "state function" property of the entropy.

ANALYSIS OF MOLECULAR COLLISIONS: AN INFORMATION-THEORETIC APPROACH by R. D. Levine
WIS-TCI-495 (supported by NASA) 13 July 1973
Published in Proceedings VIII ICPEAC (1973).

DIATOMIC INTERHALOGENS: SYSTEMATICS AND IMPLICATIONS OF SPECTROSCOPIC INTERATOMIC POTENTIALS AND CURVE CROSSINGS by M. S. Child and R. B. Bernstein
WIS-TCI-497 (Supported by NASA) 20 July 1973
This manuscript has been accepted for publication in the Journal of Chemical Physics

ABSTRACT

Spectroscopically-derived potential curves for the low-lying excited states of the homonuclear and heteronuclear diatomic interhalogens are systematized by taking cognizance of the spin-orbit state of the

dissociation products. Observed regularities lead to the prediction of a bound $B(^3\Pi_{o+})$ state of F_2 with $r_e' \simeq 1.9$, Å, $D_e' \simeq 3300$ cm^{-1}. Several of the heteronuclear interhalogens show evidence of a strong interaction between the $B(^3\Pi_{o+})$ state and a repulsive $Y(0^+)$ state, leading to the formation of a new $B'(0^+)$ state. An analysis of these interactions has led to the construction of sets of diabatic potentials consistent with the best estimated adiabatic curves, and thus to the determination of the crossing points r_x and interaction strengths $V_{12}(r_x)$. The pattern of $V_{12}(r_x)$ values suggest that they depend mainly upon the spin-orbit coupling constant of the excited atomic dissociation product. Reported also are repulsive segments of potential curves deduced for the $Y(0^+)$ states, for a series of $^1\Pi$ states and a few higher-lying (Z) states, the latter two series from analysis of existing continuum absorption data. Repulsive interactions in all four families of states studied ($^3\Pi_{o+}$, $^1\Pi_1$, $Y(0^+)$ and Z) show clear regularities governed by steric effects. Implications of the present results with respect to the theory of interatomic forces, predissociation phenomena and the scattering of ground state halogen atoms are discussed.

CLASSICAL TRAJECTORY STUDY OF THE K + CH_3I REACTION by R. A. LaBudde, P. J. Kuntz, R. B. Bernstein, and R. D. Levine
WIS-TCI-498 (supported by NASA) 1 August 1973
This manuscript has been accepted for publication in the Journal of Chemical Physics.

ABSTRACT

Classical trajectory calculations have been carried out in an attempt to simulate the reactive scattering of K by RI (R ≡ CH_3). Several semi-empirical 3-body potential surfaces have been explored. An

electron-jump surface of the covalent-ionic type, with considerable "repulsive energy release," accounts for most of the gross features of the scattering behavior. In particular, it has provided an understanding of the maximum in the reactive cross section $\sigma_R(E)$ for the exchange reaction, which can be attributed to recrossing from the ionic to the covalent region of the potential. The present calculations also predict the onset (above 2.5 eV) of collision-induced dissociation (CID), and show the conservation of total reaction cross section as CID takes over from the exchange reaction.

MOLECULAR COLLISIONS XXI. SEMICLASSICAL APPROXIMATION TO ATOM-SYMMETRIC TOP ROTATIONAL EXCITATION by Dennis Russell and C. F. Curtiss
WIS-TCI-499 (supported by NASA and NSF) 24 August 1973
This manuscript has been accepted for publication in the Journal of Chemical Physics

ABSTRACT

In Paper XIX of this series a distorted wave approximation to the T matrix for atom-symmetric top scattering was developed which is correct to first order in the part of the interaction potential responsible for transitions in the component of rotational angular momentum along the symmetry axis of the top. A semiclassical expression for this T matrix is derived by assuming large values of orbital and rotational angular momentum quantum numbers.

DEGENERATE R-S PERTURBATION THEORY by Joseph O. Hirschfelder and Phillip R. Certain
WIS-TCI-500 (supported by NASA and NSF) 10 August 1973
This manuscript has been accepted for publication in the Journal of Chemical Physics

ABSTRACT

A concise, systematic procedure is given for determining the Rayleigh-Schrödinger energies and wavefunctions of degenerate states to arbitrarily high orders even when the degeneracies of the various states are resolved in arbitrary orders. The procedure is expressed in terms of an iterative cycle in which the energy through the (2n+1)st order is expressed in terms of the partially determined wavefunction through the n-th order. Both a direct and an operator derivation are given. The two approaches are equivalent and can be transcribed into each other. The direct approach deals with the wavefunctions (without the use of formal operators) and has the advantage that it resembles the usual treatment of non-degenerate perturbations and maintains close contact with the basic physics. In the operator approach, the wavefunctions are expressed in terms of infinite order operators which are determined by the successive resolution of the space of the zeroth order functions. The operator treatment has some similarity to that of Choi (1969), but it is more closely related to that of either Hirschfelder (1969) or Silverstone-Holloway (1971). The operator expressions are useful for: double perturbations, expectation values of physical properties, and problems involving finite dimensional Hilbert space (for example, wavefunctions approximated by linear basis sets). The use of variational principles for degenerate perturbation problems is discussed.

ADDITIONAL PUBLICATIONS DURING THE PERIOD

1 JULY 1973 - 31 DECEMBER 1973

EHRENFEST'S THEOREM AND THE (GENERALIZED) TRK SUM RULE FOR VARIATIONAL WAVEFUNCTIONS
by Saul T. Epstein
J. Chem. Phys. 58, 5184-5185 (1973)

ON THE DIPOLE MOMENT OF CO^+
by Phillip R. Certain and R. Claude Woods
J. Chem. Phys. 58, 5837-5838 (1973)

EXTENDED DIATOMICS IN MOLECULES CALCULATIONS
by E. Steiner, P. R. Certain, and P. J. Kuntz
J. Chem. Phys. 59, 47-55 (1973)

CALCULATIONS AND ESTIMATES OF THE GROUND STATE ENERGY OF HELIUM TRIMERS
by L. W. Bruch and Ian J. McGee
J. Chem. Phys. 59, 409-413 (1973)

MOLECULAR COLLISIONS. XIX. THE DISTORTED WAVE APPROXIMATION TO ATOM-RIGID SYMMETRIC TOP ROTATIONAL EXCITATION
by Dennis Russell and C. F. Curtiss
J. Chem. Phys. 59, 1974-1983 (1973)

ELECTROSTATIC HELLMANN-FEYNMAN THEOREM APPLIED TO LONG-RANGE INTERATOMIC FORCES. THE HYDROGEN MOLECULE
by Erich Steiner
J. Chem. Phys. 59, 2427-2429 (1973)

DOPPLER BROADENING EFFECT ON COLLISION CROSS SECTION FUNCTIONS: DECONVOLUTION OF THERMAL AVERAGING
by R. B. Bernstein
Comments on Atomic and Molecular Physics 43-51 (1973), Vol. 4, No. 2

ON THE NONITERATIVE SOLUTION OF INTEGRAL EQUATIONS FOR SCATTERING OF ELECTROMAGNETIC WAVES
by Donald J. Kouri
J. Math. Phys 14, 1116-1120 (1973)

ANALYSIS OF ENERGY DISPOSAL: THERMODYNAMIC ASPECTS OF THE ENTROPY DEFICIENCY OF A PRODUCT STATE DISTRIBUTION
by R. D. Levine and R. B. Bernstein
Chem. Phys. Lett. 22, 217-221 (1973)

CLASSICAL STUDY OF ROTATIONAL EXCITATION OF A RIGID ROTOR: $Li^+ + H_2$. II CORRESPONDENCE WITH QUANTAL RESULTS
by R. A. LaBudde and R.B. Bernstein
J. Chem. Phys. 59, 3687-3691 (1973)

SUMMARY OF EXPENDITURES AND UNLIQUIDATED COMMITMENTS

Theoretical Chemistry Institute Portion of NASA Grant NGL 50-002-001

1 July 1973 - 31 December 1973

Salaries	$25,066.83
Computing Costs	5,786.56
Travel	-----
Publications	3,625.29
Services	819.93
Supplies	346.99
Communications	37.50
Honoraria for Consulting & Lecturing	339.06
Total Direct Costs	$36,022.16
Overhead*	7,204.43
Total Costs	$43,226.59

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* 20% of Total Direct Costs